66966-72-1; **10**, 66966-73-2; **13a**, 66966-74-3; **13b**, 66966-75-4; **14a**, 66966-59-4; **14b**, 66966-60-7; **15a**, 66966-76-5; **15b**, 60073-28-1; **15c**, 57291-16-4; **16a**, 66966-61-8; **16b**, 66966-62-9; **16c**, 66966-63-0; **17a**, 66966-65-2; **17b**, 66966-66-3; **17c**, 66966-67-4; **18**, 66966-77-6; **19**, 66966-64-1; **20**, 66966-68-5; **21a**, 66966-78-7; **21b**, 66966-79-8; **22**, 66966-80-1; azetidine, 503-29-7; piperidine, 110-89-4; dimethylamine HCl, 506-59-2; methylamine HCl, 593-51-1; aniline, 62-53-3; *m*-nitrobenzaldehyde, 99-61-6; salicylaldehyde, 90-02-8.

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Photochemistry of 2-Acetyl-3-phenylnorbornanes: Influence of a β-Phenyl Group on Carbonyl Reactivity in Relation to the Geometry of Both Chromophores

Jacqueline Moron and Georges Roussi*

Institut de Chimie des Substances Naturelles, CNRS, 91190 Gif sur Yvette, France

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The photochemistry of *trans*- and *cis*-2-acetyl-3-phenylnorbornanes *exo*-**3** and **5** and *endo*-**4** and -**6** has been investigated and compared to that of *exo*-acetylnorbornane (**1**) and the endo isomer **2**. The trans, exo compound **3** led exclusively to the Norrish type I photoproducts via the triplet state, while the cis isomer was inert. The endo compounds **4** and **6** underwent the type II photoelimination exclusively from the singlet state, and cyclization from both the singlet and the triplet. It has been shown that deactivation of excited states of carbonyl compounds by the phenyl group in both exo and endo isomers occurs only when the two chromophores are in the cis position.

The photoreactivity of formally nonconjugated phenylcarbonyl compounds has been the subject of some recent investigations.[1,2] Thus, it was shown by Whitten[2] that β-phenyl ketones with an available γ hydrogen undergo type II photoelimination as the only significant reaction. This author showed that while the triplet state is formed in good yields it returns exclusively to the ground state. The reaction occurs exclusively from the singlet state. The kinetic data obtained with somewhat rigid ketones allowed Whitten to suppose a through-space coupling between the two chromophores. Sauers,[3] studying the two isomeric 2-acetylbenzonorbornanes, reported that the exo isomer undergoes a nonefficient type I cleavage, while the endo isomer is photostable. The author suggested that the proximity of the two chromophores in the latter provides a channel for radiationless decay of the triplet.

It therefore appeared attractive to us to study rigid systems with an available γ hydrogen in order to investigate the influence of the phenyl group on carbonyl reactivity in relation to the relative geometry of both chromophores. Thus, the four isomeric acetylphenylnorbornanes **3**, **4**, **5**, and **6** were synthesized and their photochemical reactivity was compared to the acetylnorbornanes **1** and **2**. The photochemistry of the latter had not been studied before.

We report first that the behavior of the methyl ketones **1** and **2** was entirely different from that of the corresponding aryl ketones.[4] Secondly we show that the phenyl group exerts its influence only in the cis isomers **4** and **6**. Finally, we demonstrate that the Norrish type I reaction was more subject to the influence of the phenyl group than the γ hydrogen abstraction reaction.

Results

I. Product Study. The structures of the products were assigned on the basis of their spectral data and by chemical correlation in the case of ketone **13**.[5]

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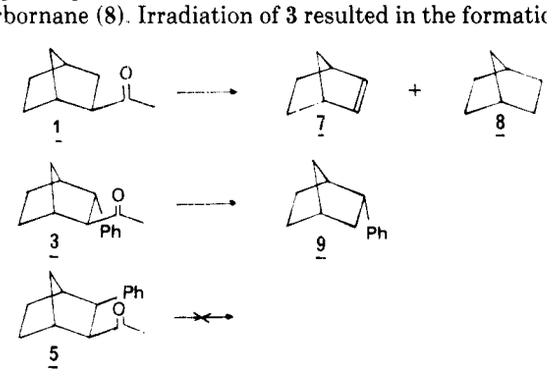
Table I. ^{13}C NMR and ^{1}H NMR Data Used in the Assignment of the C_4 Stereochemistry in Compounds 11, 14, and 15

	^{13}C NMR, δ		^{1}H NMR, δ		
	Me	C_4	Me	H_6	H_2
11a	19.5	79.1	1.1	3.1	
11b			1.3	>2.3	
14a	20.1	78.9	1.2	3.2	2.9
14b	27.9	70.6	1.4	2.4	3.3
15	22.3	79.5	0.4	3.3	

The C_4 stereochemistry of the two isomers (a and b) of the alcohol **14** was assigned on the basis of comparison of their ^{1}H NMR and ^{13}C NMR spectra (Table I). Compound **14a** possesses a methyl group which is more hindered than in **14b**. Its ^{13}C resonance was therefore found at higher field (20.1 ppm) than the similar carbon atom in **14b** (27.9 ppm). The same phenomenon was observed in the ^{1}H NMR spectrum for the methyl protons (respectively δ 1.2 in **14a** and δ 1.4 in **14b**). In addition, H_6 is more shielded in **14a** (δ 3.2) than in **14b** (δ 2.4)[6] and there was a marked difference in the position of the resonance for the benzylic protons H_2 in the two isomers, these effects being due to the influence of the hydroxylic group.[7] Similar H_6 shifts in the ^{1}H NMR spectra of **11a, 14a,** and **15** were observed. The same trend was noted for the methyl group shift in ^{13}C NMR and ^{1}H NMR spectra.

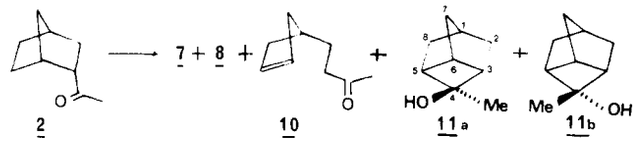
These results show that **11a, 14a,** and **15,** which are the major isomers formed by irradiation, possess the same C_4 stereochemistry, whereas **11b** and **14b** have the opposite C_4 configuration. It must be noted that the **14b** quaternary carbon C_4 signal in the ^{13}C NMR spectrum was surprisingly deshielded relative to that for **14a.** Contrary to the acyclic β-phenyl ketones described by Whitten,[2] compounds **3, 4, 5,** and **6** show fluorescence emission in acetonitrile. The phosphorescence spectra of those ketones taken at 77 K permitted the evaluation of their triplet energy (~ 74 kcal/mol).

A. Photochemistry of the Exo Isomers 1, 3, and 5. In acetonitrile *exo*-1-acetylnorbornane (**1**) was observed to undergo complete conversion to a mixture of norbornene (**7**) and norbornane (**8**). Irradiation of **3** resulted in the formation of



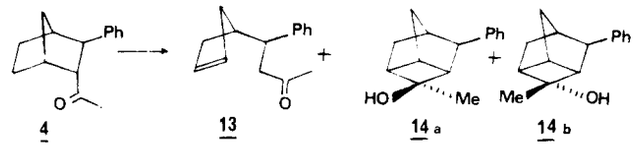
endo-phenylnorbornane (**9**), while the exo,cis isomer **5** proved to be quite stable under irradiation.

B. Photochemistry of the Endo Isomers 2, 4, and 6. *endo*-1-Acetylnorbornane underwent three types of reaction: Norrish type I (NI) (leading to **7** and **8**), Norrish type II (NII) photoelimination (leading to **10,** which disappeared upon

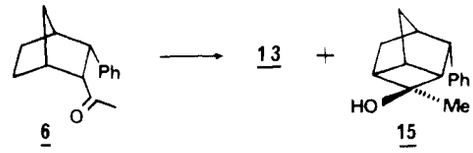


prolonged irradiation), and photocyclization [leading to the two isomers (a and b) of 4-methyltricyclo[3.2.1.$0^{3,6}$]octan-4-ol (**11**)].

Irradiation of *endo*-2-acetyl-3-phenylnorbornane (**4**) resulted in the formation of the photoelimination product **13** and to the mixture of the two isomers (a and b) of the tricyclic alcohol **14.**



Endo,cis isomer **6** underwent photoelimination (leading to **13**) and photocyclization, which gave only one isomer of the tricyclic alcohol **15.**



II. Mechanistic Studies. Degassed 0.01 M solutions of ketones **1–6** contained in UV cells were irradiated by a 313-nm line produced by a monochromator. Light intensities were measured by ferrioxalate actinometry. Product yields were determined by analytical VPC for conversion of <10% in acetonitrile solutions. The quantum yields (Φ) are given in Table II. The reactivity of ketones **1–6** was also investigated in the presence of high concentrations (0.2 M) of *cis*-1,3-pentadiene (piperylene), and the quantum yields (Φ_q) were determined. No quenching of the type II elimination process occurred in **2, 4,** or **6** at concentrations up to 0.6 M.

Linear Stern–Volmer plots for quenching of alcohols **11, 14,** and **15** could not be obtained owing to the very small value of their quantum yield formation, but were obtained for quenching of norbornane (**8**) from the endo ketone **2** and phenylnorbornane (**9**) from **3.**

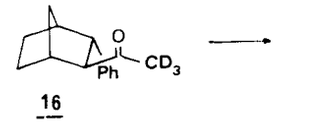
The quantum yields for triplet sensitized cis–trans isomerization of piperylene by the different ketones were measured as a function of diene concentrations. Good correlation of $1/\Phi_{c\rightarrow t}$ vs. 1/[diene] was obtained for every ketone except **1.** From these plots, the triplet lifetimes (τ_T) and intersystem crossing quantum yields (Φ_{isc}) were obtained.[8] In the case of **1** the lack of correlation was possibly due to a consumption of piperylene by ketone.

Quantum yields of sensitized reactions (Φ_{sens}) were determined in acetonitrile–acetone mixture)1 M).[9]

All the results are summarized in Table II.

Discussion

I. Photochemical Behavior of *exo*- and *endo*-Acetylnorbornane (1 and 2). A. *exo*-Acetylnorbornane (1) in Acetonitrile. The exo ketone bearing a γ hydrogen gave **7** and **8** essentially via the ketone triplet state.[12] The formation of this saturated compound was unusual in the NI reaction. However, Sauers[3] obtained this type of compound after irradiation of acetylbenzoylnorbornane. Sauers[3] considered that the hydrogen originates from a radical pair disproportionation, giving the saturated compound and ketene, rather than from the solvent used (cyclohexane). We tested this possibility using the trideuterated ketone **16.** The recovered saturated



product was found to contain no deuterium. We concluded that acetonitrile (a poor hydrogen-donating solvent) was the hydrogen source, this being allowed by the unusually high degree of strain associated with a norbornene double bond

Table II. Quantum Yields and Quenching Data[i]

starting compd	product	Φ	Φ_{sens}	Φ_q	$\Phi_{t\text{-BuOH}}$[a]	Φ_{isc}	τ, s[b]
1	7	0.024 ± 0.005				0.9	2×10^{-9}
	8	0.64 ± 0.1	0.014 ± 0.002	0.014[c] ± 0.003			
3	9	0.28 ± 0.07	0.05 ± 0.005			1	6×10^{-9}
5						0.7	2×10^{-8}
2	7	0.0038 ± 0.0005				0.2	1.8×10^{-8}
	8	0.14 ± 0.01	0	0			
	10	0.096 ± 0.01	0	0.10[d] ± 0.01	0.12 ± 0.01		
	11a,b	0.026 ± 0.001	0.006 ± 0.001	0.020 ± 0.001	0.027 ± 0.002		
4	9					0.3	5×10^{-9}
	13	0.22[e] ± 0.05	0.058 ± 0.005	0.23 ± 0.02			
	14a,b	0.024[f] ± 0.005	0.19[g] ± 0.04	0.007 ± 0.001	0.0079		
6	13	0.059 ± 0.004	0.0034 ± 0.0005	0.055 ± 0.005	0.04	0.2	9×10^{-9}
	15	0.012[h] ± 0.001	0.027 ± 0.005	0.004 ± 0.001	0.01 ± 0.001		

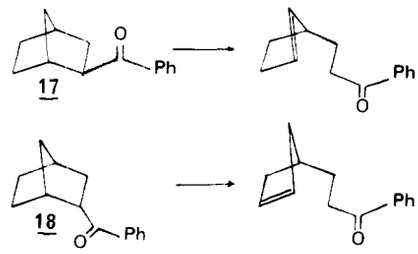
[a] Quantum yields were determined in a 2:1 mixture of acetonitrile–*tert*-butyl alcohol.[10] Added *t*-BuOH had no influence on the results obtained in acetonitrile, due to an insufficient difference in polarity between the two solvents. [b] Calculated from slope of $1/\Phi_{c\to t}$ vs. 1/[diene] taking $k_q(CH_3CN) = 2.9 \times 10^{10}$ L/mol · s.[11] [c] Up to 0.6 M in piperylene. [d] The photolabile ketone **10** was stable in the presence of piperylene, which explains the higher quenched quantum yields observed and results in its preparation in a very good yield. [e] This value is approximate, since **13** was not completely stable under irradiation. [f] The ratio **14a/14b** in acetonitrile (3.2) and in an acetonitrile–acetone mixture (3.2) was determined after purification by column chromatography. [g] This result is incompatible with the intersystem crossing quantum yield. A possible explanation could be that acetone, which is used in large excess, generates important solvent effects. [h] The formation of the single hindered isomer of the alcohol **15** in this reaction was not surprising if one considers that there was a solvation of the biradical intermediate, which prevented the cyclization leading to the *endo*-hydroxyl group isomer. [i] Registry no.: **1**, 824-59-9; **2**, 824-58-8; **3**, 67271-49-2; **4**, 67335-59-5; **5**, 67335-58-4; **6**, 67335-60-8; **7**, 498-66-8; **8**, 279-23-2; **9**, 17989-94-5; **10**, 60443-42-7; **11a**, 67271-50-5; **11b**, 67335-61-9; **13**, 67271-51-6; **14a**, 67271-52-7; **14b**, 67335-62-0; **15**, 67335-63-1.

Table III. Ratios of the Isomeric Alcohols 11 According to the Carbonyl Excited States

	CH_3CN	*t*-BuOH	CH_3CN + piperylene	CH_3 + acetone
11a + 11b	0.026	0.027	0.020	0.006
11a	0.021	0.021	0.017	
11b	0.0056	0.006	0.003	
11a/11b	3.8	3.5	5.1	1.7

formation. As expected, the norbornene quantum yield in benzene (a very poor hydrogen donating solvent) was greater (0.24) than in acetonitrile.[12b]

B. Comparison between *exo*-Acetylnorbornane (1) and *exo*-Benzoylnorbornane (17).[4] The behavior of ketone 1 was different from that of the corresponding aryl ketone (**17**)



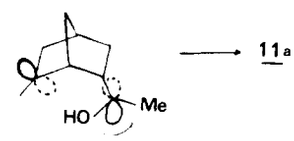
studied by Lewis,[4] which gave exclusively type II photoelimination in benzene.

Lewis showed that NII was much more efficient in the endo isomer **18** than in the exo isomer **17** [k_γ**18**/**17**) = 500] and that this reflects conformational or stereoelectronic requirements for γ-hydrogen abstraction. The rigid bicycloalkane structure allows the carbonyl oxygen to come within 1.7 Å of the endo γ-H and more than 2.2 Å in the exo isomer.[4]

The same steric requirements exist in the *exo*-**1** isomer, which follows the NI pathway. We think that this photochemical behavior could be explained through energy considerations. The triplet energy of the excited ketones **1** and **3** (~78 kcal/mol) is located on a chromophore (–$COCH_3$) and is high enough to break the C–C bond. The triplet energy of aromatic ketone is much lower and spread over a larger chromophore (–COPh), which does not allow C–C bond rupture: γ-hydrogen abstraction is then the preferred reaction pathway followed by these ketones.[26] A result favoring this hypothesis was obtained with the exo ketone **3** (triplet energy ~74 kcal/mol). Here again, only the NI reaction was observed, but with a lower efficiency (0.28) than in ketone **1**.

C. Photochemical Behavior of *endo*-Acetylnorbornane (2). Photoelimination and cyclization reactions compete with the Norrish type I due to the favorable conformation for γ-H abstraction. The elimination reaction occurs almost exclusively from the singlet excited state and could not be sensitized by acetone.[9] In the cyclization reaction, however, a slight sensitization by acetone was possible. It must be pointed out that we observed a variation in the ratio of the isomeric alcohols **11**, depending on the carbonyl excited state (1.7 in the triplet state and 5.1 in the singlet state in acetonitrile in the presence of piperylene) (Table III).

The same stereoselectivity originating from the singlet excited state has already been observed by Turro[14] in the photocyclization of 1-adamantylacetone. This observation was consistent with a singlet short-lived biradical undergoing rehybridization on the γ-C resulting in a preferential rotation and closure to **11a**. The absence of stereoselectivity in the



triplet state may be due to the longer triplet biradical lifetime which could attain its preferential conformation before closure (cf. ref 14).

II. Phenyl Group Influence on Carbonyl Reactivity in Correlation with Relative Geometry of Both Chromophores in Ketones 3–6. A. Triplet Deactivation. Ketones **3–6** allow one to compare in the same system the three classical types of intramolecular ketone reactions, i.e., NI, NII, and photocyclization. As shown in Table II, the greatest influence of the β-phenyl group was observed for the type I reaction. Thus, norbornane (**8**) was formed essentially from the triplet either from the *exo*-**1** or *endo*-**2** isomer with good quantum

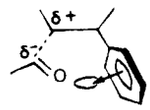
yields (respectively 0.64 and 0.14). For the *trans,exo*-acetylphenylnorbornane (**3**), the reaction was purely triplet but the quantum yield formation of **9** was lower (0.28). As before, we attributed this smaller value to the lower triplet energy level of the β-phenyl ketone relative to **1**. In the trans,endo ketone **4**, the type II and cyclization reactions are favored, since practically no NI product was detected. For the cis isomers neither *exo*-**5** nor *endo*-**6** underwent type I reaction, although their triplet is formed in good yield.

NII elimination occurs mostly via the singlet state, but sensitizing experiments showed that there was a greater participation of the triplet state in the trans isomer **4** (Φ_{sens}/Φ = 0.27) than in the cis isomer **6** (Φ_{sens}/Φ = 0.057).

Quenching experiments showed that photocyclization reactions occurred mostly via the triplet state of excited ketones. As in the NI and NII reactions, we observed a deactivation of those triplets only for the cis isomers (**11**, Φ = 0.026; **14**, Φ = 0.024; **15**, Φ = 0.012).

These results show that a considerable through-space interchromophoric coupling exists which provides a channel for rapid radiationless deactivation of the triplet. Such a coupling has been proposed by Whitten[2] and by Wagner and Sternitz in the β-phenyl aromatic ketones.[1b,c] This coupling could proceed via a *n*-type exciplex as proposed in the case of the benzophenone triplet quenching by aromatic solvents.[15] The radiationless deactivation of this exciplex leads to the ground-state molecule, and the cis geometry of **5** and **6** offers very favorable conditions for its formation. Thus ultraviolet spectra of these compounds showed important perturbations which are not observed in the trans isomers **3** and **4**, for which there is no possibility of such coupling (see Experimental Section). In acyclic β-phenyl ketones there is no important phenyl–carbonyl interactions in the ground state.[1a] However these take place in the excited state, implying preferential conformations for orbital overlap of the two chromophores.

It appears that γ-hydrogen abstraction by excited triplet ketone is not completely prevented by the *cis*-β-phenyl group, contrary to the Norrish I reaction. This fact could be due to a difference in activation energy between the two reactions. An alternate explanation could be that there is considerably more ionic character in the transition state for the NI reaction than for γ-hydrogen abstraction in alkanones, as in the case of aromatic ketones.[16]



The *n*-type exciplex tends to prevent bond breaking and thus disfavors the NI reaction, since the half-filled n orbital of the ketone is directed toward the aromatic electrons.

B. Singlet Deactivation. As shown in Table II, the major reaction pathway observed for the endo isomer occurs in the *singlet state*. Here again, we only observed a quantum yield decrease for the cis isomer (Φ in **2** = 0.096; in **4** = 0.22; in **6** = 0.059). This nonradiative decay from singlets of β-phenyl ketones in the course of the NII elimination has been extensively studied by Whitten in acyclic ketone systems.[2] This author concluded that there is significant through-space coupling between the two chromophores in the singlet state. Our comparative results obtained with endo ketones **4** and **6** agree with this type of coupling as in the triplet manifold.

III. Intersystem Crossing Quantum Yields in Acetylnorbornane Derivatives. Our results showed that there was a striking difference in the Φ_{isc} value between the *exo*-**1** (0.9) and *endo*-**2** (0.2) isomers. The decrease observed could be due to the availability of the γ-H in the endo ketone, which resulted in an increase in chemical reactivity from the singlet state and in radiative or nonradiative decay from this state.[17] The presence of a phenyl group in the cis or trans endo ketones **4** and **6** resulted in no change in the Φ_{isc}. In the exo compounds **3** and **5**, in which γ-H is less available, the low Φ_{isc} value (0.6) observed in the cis compound is due to the proximity of the phenyl group, which offers a different deactivating process from the singlet state (via the *n*-type exciplex).

Summary

The system studied has allowed us to compare the intramolecular influence of a phenyl group on the carbonyl reactivity of the three types of ketone photoreactions: NI, photoelimination, and photocyclization. Nothing was known about the phenyl influence on the latter.

It has been shown that deactivation of both singlet and triplet excited states occurs only when the two chromophores are in the cis position. This geometry favors the *n*-type exciplex formation, which provides a way for rapid radiationless deactivation of excited states. Finally, it has been found that NI is more subject to the presence of the *cis*-phenyl group than photocyclization, the other triplet reaction.

Experimental Section

Infrared spectra (IR) were determined in $CHCl_3$ solutions on a Perkin-Elmer Model 257 spectrometer; ultraviolet (UV) spectra were recorded on a Bausch and Lomb Spectrometric 505, in ethanol as solvent. Nuclear magnetic resonance (NMR) data were obtained from a Varian Model T60 or a Perkin Elmer R12 spectrometer in CCl_4 or $CDCl_3$ solutions. ^{13}C nuclear magnetic resonance (^{13}C NMR) spectra were obtained on a Brucker HFX-90 MHz NMR spectrometer in $CDCl_3$ solutions. Chemical shifts are reported in δ (ppm) from the internal standard Me_4Si. Mass spectra (MS) were recorded on a MS9 spectrometer. Vapor-phase chromatograms (VPC) were obtained from a Girdel 75 model on the following columns: A, 5% OV_1 (300 × 0.6 cm); B, 8% QF_1 (300 × 0.6 cm); C, 20% ββ′-ODPN (300 × 0.6 cm). Relative retention times (t_R) refer to the ratios of retention times of formed products to the corresponding starting product. Analyses were carried out in the Service Central de Microanalyse du CNRS. Melting points were uncorrected. All experiments were carried out under nitrogen.

***exo*-2-Acetylnorbornane (1)** was prepared according to Stockmann.[18] Pure product (4.6 g, 33 mmol, 67%) was obtained after chromatography on silica gel (5% ether in pentane) from 4.6 g of norbornene (49 mmol): UV λ_{max} 280 nm (ε 27); NMR ($CDCl_3$) δ 2.16 (s) in a multiplet between 2.0 and 2.8 (5 H), 1–1.9 (m, 9 H); ^{13}C NMR δ 28.7 (q, Me), 29.0, 29.9 (t, C_5, C_6), 32.5 (t, C_3), 36.0 (t, C_7), 36.2 (d, C_4), 40.0 (d, C_1), 55.0 (d, C_2), 209.0 (s, C=O).

***endo*-2-Acetylnorbornane (2).** *endo*-2-Norbornanecarboxylic acid (2.97 g, 21.2 mmol), prepared according to the literature,[19] was treated with MeLi in anhydrous ether. Workup and chromatography on silica gel (5% ether in pentane) gave 2.1 g (15.2 mmol, 72%) of **2**:[20] UV λ_{max} 280 nm (ε 24); NMR ($CDCl_3$) δ 2.08 (s) in a multiplet between 1.0 and 2.1 (12 H), 2.2–3 (m, 2 H); ^{13}C NMR δ 24.5 (t, C_6), 29.1, 29.7 (t, C_5–C_3), 29.6 (Me), 37.2 (d, C_4), 40.4 (d, C_1), 40.7 (t, C_7), 54.8 (d, C_2), 210.0 (s, C=O).

***exo*-2-Acetyl-*endo*-3-phenylnorbornane (3).** *endo*-3-Phenylnorbornene-2-*exo*-carboxylic acid (4.2 g, 19.8 mmol), prepared according to the literature,[21] was dissolved in 70 mL of anhydrous ether in a three-neck flask equipped with a magnetic stirrer, reflux condenser, and a dropping funnel. Methyllithium (40 mmol) in anhydrous ether was added dropwise. The mixture was stirred for 0.5 h and hydrolyzed by the addition of saturated NH_4Cl solution. Extraction and usual treatments furnish 4 g of crude product which was purified on alumina column chromatography (10% benzene in pentane) to yield 3.1 g (14.4 mmol, 73%) of unsaturated product, *exo*-2-acetyl-*endo*-3-phenylnorbornene: NMR (CCl_4) δ 1.5 (br d, 2 H), 2.1 (s, 3 H), 2.5 (br d, 1 H), 3 (m, 2 H), 3.5 (m, 1 H), 6 (m, 1 H), 6.5 (m, 1 H).

Hydrogenation in MeOH over PtO_2 of 1 g (4.7 mmol) of unsaturated ketone gave 0.94 g (4.39 mmol, 93%) of **3**: UV λ_{max} 258 (ε 250), $\lambda_{n\pi^*}$ 280 nm (ε 53); NMR (CCl_4) δ 1.3 (m, 6 H), 2 (s, 3 H), 2.5 (m, 3 H), 3.4 (m, 1 H), 7.2 (s, 5 H); ^{13}C NMR δ 22.6, 29.9 (t, C_6, C_5), 29.1 (Me), 38.3 (t, C_7), 41.2, 42.7 (C_1, C_4), 48.3, 59.2 (d C_3, C_2), 126.2, 128.2, 128.3, 141.6 (aromatic carbons), 209.1 (s, C=O); MS (*m/e*) 214 (M^+), 171, 147, 43. Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.67; O, 7.47. Found: C, 83.90; H, 8.36; O. 7.48.

***endo*-2-Acetyl-*exo*-3-phenylnorbornane (4).** The corresponding carboxylic acid (430 mg, 2 mmol), prepared according to the literature,[21] was treated with $(COCl)_2$ in anhydrous benzene. The resulting

acid chloride was added at −78 °C to an ethereal solution of dimethylcopper reagent prepared according to the literature.[22] Crude product **4** (370 mg) was obtained after hydrolysis at −78 °C and usual chromatographic workup chromatographic over alumina (ether 1% in pentane) gave 274 mg (1.28 mmol, 64%) of pure product **4**: UV λ_{max} 258 (ϵ 246), $\lambda_{n\pi^*}$ 280 nm (ϵ 58); NMR (CCl_4) δ 1.4 (m, 6 H), 2.0 (s, 3 H), 2.6 (m, 3 H), 3.1 (m, 1 H), 7.0 (s, 5 H); ^{13}C NMR δ 23.9, 30.1 (t, C_6, C_5), 29.6 (Me), 38.9 (t, C_7), 41.0, 42.7 (d, C_1, C_4), 46.4, 64.8 (d C_3, C_2), 125.8, 126.9, 128.5, 146.4 (aromatic carbons), 208.7 (s, C=O); MS 214 (M^+), 171, 77, 43. Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.67; O, 7.47. Found: C, 83.82; H, 8.50; O, 6.95.

***exo*-2-Acetyl-*exo*-3-phenylnorbornane (5).** Prepared from 127 mg (0.59 mmol) of the corresponding carboxylic acid[21] and treated as described above. Chromatography over alumina (ether 1% in pentane) gave 87 mg (0.41 mmol, 69%) of pure product **5**: UV λ_{max} 260 (ϵ 190), $\lambda_{n\pi^*}$ 280 nm (ϵ 20); NMR (CCl_4) δ 1.3 (s) in a multiplet centered at 1.4 (8 H), 2.3 (m, 3 H), 2.9 (m, 2 H), 7.2 (s, 5 H); ^{13}C NMR δ 28.5, 31.2 (C_5, C_6), 29.4 (Me), 37.1 (t, C_7), 38.5, 43.6 (d, C_1, C_4), 52.7, 62.6 (d, C_3, C_2), 126.5, 128.0, 128.3, 142.5 (aromatic carbons), 209.9 (s, C=O); MS (*m/e*) 214 (M^+), 171, 147, 77, 43. Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.67; O, 7.47. Found: C, 83.85; H, 8.49; O, 7.54.

***endo*-2-Acetyl-*endo*-3-phenylnorbornane (6)** was prepared from 600 mg (2.75 mmol) of the corresponding cis carboxylic acid,[21] care being taken of the following steps. MeLi was freshly prepared and titrated in such a way to avoid its excess (negative Gilman's test). Hydrolysis of the reaction mixture was run at −78 °C with theoretical amounts of aqueous 5% H_2SO_4. Chromatography on silica (ether 2% in pentane) gave 380 mg (1.77 mmol, 64%) of **6** containing 4% of trans isomer **3** (VPC column B): UV λ_{max} 260 nm (ϵ 400), $n\pi^*$ disappears in $\pi\pi^*$ absorption; NMR (CCl_4) δ 1.5 in a broad multiplet centered at 1.4 (9 H), 2.4 (m, 2 H), 3 (m, 1 H), 3.7 (m, 1 H), 7.3 (m, 5 H); ^{13}C NMR δ 23.1, 23.3 (br s, C_5, C_6), 30.6 (q, Me), 39.4, 44.4 (d, C_1, C_4), 40.2 (t, C_7), 47.6, 57.8 (d, C_3, C_2), 126.1, 127.2, 127.8, 128.1, 128.6, 140.4 (aromatic carbons), 210.2 (s, C=O); MS (*m/e*) 214 (M^+), 171, 147, 43. Correct elemental analyses could not be obtained with this compound owing to its lability.

***exo*-2-Acetyl-d_3-*endo*-3-phenylnorbornane (16).** Prepared from 138 mg (0.64 mmol) of the corresponding carboxylic acid[21] by action of $(CD_3)_2CuLi$ in the conditions described above. Chromatography on silica gel (ether 2% in pentane) gave 96 mg (0.44 mmol, 69%) of **16**. The NMR spectrum was practically identical with that of **3**, exception being made of the singlet at δ 2 (3 H); MS (*m/e*) 217 (M^+), 171, 46.

4-Cyclopentyl-4-phenyl-2-butanone (12). Anhydrous THF (10 mL) was added to 10 mmol of cyclopentylmagnesium bromide in ether. The solution was added dropwise to a well-stirred mixture of 0.7 g (5 mmol) of *trans*-4-phenyl-3-buten-2-one and 28 mg (0.15 mmol) of CuI in anhydrous THF. After 2 h at room temperature, hydrolysis, and usual treatment, 1 g of crude product was obtained. Chromatography on SilicAR CC-4 (benzene 25% in pentane) gave 352 mg (1.64 mmol, 33%) of pure product: NMR (CCl_4) δ 1.8 (s) in a broad multiplet between 1 and 2 (12 H), 2.6 (m, 3 H), 7.1 (5 H); semicarbazone (EtOH) mp 152–153 °C. Anal. Calcd for $C_{16}H_{23}N_3O$: C, 71.04; H, 8.77; O, 5.57; N, 14.62. Found: C, 70.92; H, 8.68; O, 5.68; N, 14.48.

Photolyses. Preparative irradiations were carried out in a water-cooled immersion apparatus equipped either with a 450-W (Hanovia 450 W, lamp A), or a 100-W medium-pressure mercury arc (Hanau NK 6/20 100 W, lamp B). During irradiations a stream of argon was bubbled through the solutions. In the case of **3**, preparative irradiations were simply carried out in quartz tubes (lamp A) under argon atmosphere.

Irradiation of 1. A solution of 410 mg (2.3 mmol) of **1** in 280 mL of CH_3CN was irradiated for 7 h in a quartz apparatus (lamp B). VPC analysis (column A) showed almost complete disappearance of **1** and formation of two new compounds, **7** and **8**, identified by comparison of their retention times with those of authentic samples on three different VPC column (A, B, and C).

Irradiation of 2. (A) Irradiation in Acetonitrile. A solution of 480 mg (3.47 mmol) of **2** in 400 mL of CH_3CN was irradiated in a quartz apparatus (lamp B). Three photoproducts were detected by VPC (column B, 110 °C) in respective yields of **1** (**11a**, t_R = 0.49), **4** (**11b**, t_R = 0.62), and 21% (**10**, t_R = 1.22) relative to **2**. Chromatography of the crude mixture on silica gel gave 96 mg of volatile starting product **2** (ether 5% in pentane), 81 mg (0.58 mmol, 17%) of the colorless oil **10** (ether 5% in pentane), and 19 mg (0.14 mmol, 4%) of white needles **11a** (ether 30% in pentane). **10**: NMR ($CDCl_3$) δ 2.1 (s) in a broad multiplet between 1 and 3 (12 H), 5.7 (s, 2 H). **11a**: NMR ($CDCl_3$) δ 1.1 (s, 3 H), 1.1–1.8 (m, 6 H), 1.9–2.4 (m, 4 H and 3 H after deuteriation), 3.1 (m 1 H); ^{13}C NMR δ 19.5 (q, Me) 34.0 (*t*, C_2, C_8) 36.3, 39.2 (d, C_1, C_6), 38.0 (t, C_7), 45.0 (d, C_3, C_5), 79.1 (s, C_4); mp (sublimated) 94–95 °C. Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21; 0, 11.58. Found: C, 77.88; H, 10.34; 0, 11.85.

(B) Irradiation in Acetone. A solution of 526 mg (3.8 mmol) of **2** in 450 mL of acetone was irradiated in a Pyrex apparatus for 16 h. The yields of **11a** and **11b** were respectively 17 and 9% relative to the starting product **2**. Chromatography of the crude mixture on silica gel gave a mixture of starting ketone **2** and unidentified products (ether 5% in hexane), 78 mg of a fraction containing **11b** (ether 10% in hexane), and 68 mg (13%) of **11a** (ether 20% in hexane). Another chromatography gave 6 mg of the very volatile alcohol **11b**: NMR ($CDCl_3$) δ 1.3 (s) in a broad multiplet between 1.1 and 2.4 (14 H); MS (*m/e*) 138 (M^+, low intensity), 120.

Irradiation of 3. A solution of 80 mg (0.37 mmol) of **3** in 10 mL of CH_3CN was irradiated for 16 h in quartz tubes (lamp B). VPC analysis (column A) showed the presence of a single product (t_R = 0.36) with traces of other unidentified products (~2%). Chromatography over SilicAR CC-4 (pentane) gave 22 mg (0.11 mmol, 31%) of **9**; NMR identical with literature description;[23] MS (*m/e*) 172 (M^+).

Another experiment from 150 mg of **3** (0.7 mmol) in acetone as solvent and in a Pyrex tube led to 83 mg (0.48 mmol, 68%) of pure product.

Irradiations of 4. (A) Irradiation in Acetonitrile. A solution of 450 mg (2.10 mmol) of **4** in 450 mL of CH_3CN was irradiated for 4 h (lamp B). Two photoproducts were detected by VPC (column A) in yields of 47 (t_R = 0.8) and 9% (t_R = 1.2) relative to the starting product **4**. Chromatography of the crude mixture on alumina gave 110 mg (25%) of **4**, 172 mg (0.80 mmol, 38%) of **13** (benzene 10% in pentane), and 33 mg (0.15 mmol, 7%) of **14** (ether). **13**: NMR (CCl_4) δ 1.8 (s, 3 H), 1.8–3 (m, 8 H), 5.6 (s, 2 H), 7.1 (s, 5 H); MS (*m/e*) 214 (M^+), 156, 147, 77, 43. Catalytic hydrogenation of **13** over PtO_2 in MeOH gave a compound identical (IR, NMR, VPC) with **12**.

By analytical VPC (column B) it was possible to separate the two isomers of **14** (**14a/14b** ~ 3), but they were obtained in pure form only in the case of the irradiation of **4** in acetone as solvent.

(B) Irradiation in Acetone. A solution of 450 mg (2.10 mmol) of **4** in 450 mL of freshly distilled acetone was irradiated for 15 h in a Pyrex reactor (lamp B). Short retention time products coming from irradiated acetone[24] were detected by VPC (column A). The yields of **13** and **14** were respectively 2 and 77% relative to the starting product. Chromatography of the crude mixture on alumina gave unidentified products, **4** (50 mg), **13** (15 mg, 3%) (benzene 75% in pentane), and the mixture **14a** + **14b** (380 mg, 80%) (ether 10% in benzene). VPC (column B) showed **14a/14b** ~ 3. Repeated chromatography of this fraction (benzene 75% in pentane) followed by preparative TLC gave 30 mg (7%) of pure **14b**: NMR ($CDCl_3$) δ 1.4 (s) in a multiplet between 1.3 and 1.6 (4 H), 1.7 (m, 2 H, 1 H after deuteriation), 1.9 (m, 1 H), 2.4 (m, 5 H), 3.3 (s, 1 H), 7.2 (m, 5 H); ^{13}C NMR δ 27.9 (Me), 31.7, 33.4 (C_8, C_7), 35.3, 43.9 (C_6, C_1), 45.0 (C_5), 46.6, 50.8 (C_3, C_2), 70.6 (C_4), 125.5, 127.9, 128.0, 145.3 (aromatic carbons); MS (*m/e*) 214 (M^+), 196.

Elution with benzene first gave a fraction containing both **14a** and **14b**, and then pure **14a**: 96 mg (21%); NMR ($CDCl_3$) δ 1.2 (s, 3 H), 1.4 (m, 2 H), 1.7 (m, 2 H), 2–3 (m, 4 H), 2.9 (s, 1 H), 3.2 (br s, 1 H), 7.2 (m, 5 H); ^{13}C NMR δ 20.1 (q, Me) 33.9, 34.0, (t, C_8, C_7), 39.3, 43.7 (d, C_6, C_1), 44.9 (d, C_5), 49.4, 50.6 (d, C_3, C_2), 78.9 (s, C_4), 125.7, 125.8, 128.2, 144.7 (aromatic carbons); MS (*m/e*) 214 (M^+), 196; mp (pentane–ether) 68 °C. Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.67; O, 7.47. Found: C, 84.13; H, 8.46; O, 7.65.

Irradiation of 5. Ketone **5** was irradiated in different solvents (CH_3CN, acetone, *t*-BuOH). This compound was quite stable even after a long period of irradiation (20 h, lamp A).

Irradiation of 6. (A) Irradiation in Acetonitrile. A solution of 350 mg (1.6 mmol) of **6** in 300 mL of freshly distilled acetonitrile was irradiated for 16 h in a quartz reactor (lamp B). Two photoproducts were detected by VPC (column A) in yields of 47 (t_R = 0.79) and 20% (t_R = 1.1) relative to the starting product **6**. Chromatography of the crude mixture on silica gel gave 70 mg (20%) of **13** (ether 2% in pentane) and 27 mg (8%) of **15**, which crystallized into two forms (pentane–ether): NMR ($CDCl_3$) δ 0.4 (s, 3 H), 1.5 (m, 2 H), 2.2 (m, 4 H, 3 H after deuteriation), 2.8 (m, 2 H), 3.2 (m, 2 H), 7.2 (s, 5 H); ^{13}C NMR δ 22.3 (q, Me), 31.0 (t, C_8), 37.4 (t, C_7), 38.1, 41.6 (C_6, C_1), 45.6 (d, C_5), 47.8, 50.2 (d, C_3, C_2), 79.5 (s, C_4), 125.4, 127.5, 128.1, 141.7 (aromatic carbons); MS (*m/e*) 214 (M^+), 196; mp 80 and 90 °C. Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.67; O, 7.47. Found: C, 83.82; H, 8.35; O, 7.65.

(B) Irradiation in Acetone. A solution of 175 mg of **6** (0.82 mmol) in 320 mL of acetone was irradiated for 19 h in a Pyrex reactor (lamp B). The yields of **13** and **15** determined by VPC (column A) were respectively 4 and 50% relative to the starting product. A first chro-

matography of the crude mixture on silica gel gave 54 mg of **6** and 73 mg (42%) of **15**. A second chromatography (ether 5% in benzene) gave 49 mg (28%) of pure **15**.

Quantum Yield Determinations. Solutions of different ketones **1–6** ($\sim 10^{-2}$ M) in spectrograde acetonitrile or in a 1 M solution of acetone in acetonitrile were subjected to three freeze–pump–thaw cycles and sealed at 10^{-4} mm in 10-mm o.d. quartz cells. Irradiations were carried out using a 313-nm line produced by a Bausch and Lomb monochromator. Light intensities were measured by ferrioxalate actinometry. Photolyses were run to <10% conversion, and the resulting solutions were analyzed by VPC.

Quenching Studies. Sample preparations and irradiations were the same as for the quantum yield determinations except that varying amounts of *cis*-1,3-pentadiene (10^{-3} to 0.6 M) were added to the solutions. Percentages of isomerization of *cis*-pentadiene were determined on column C (room temperature).

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Registry No.—12, 67271-53-8; **12** semicarbazone, 67271-56-11; **16**, 67271-54-9; *endo*-2-norbornanecarboxylic acid, 934-28-1; *endo*-3-phenylnorbornane-2-*exo*-carboxylic acid, 59286-05-4; *endo*-2-carboxy-*exo*-3-phenylnorbornene, 58800-36-5; *exo*-2-carboxy-*exo*-3-phenylnorbornane, 59286-12-3; cyclopentyl bromide, 137-43-9; *trans*-4-phenyl-3-buten-2-one, 1896-62-4; *exo*-2-acetyl-*endo*-3-phenylnorbornene, 67271-55-0; 2-*endo*-carboxy-3-*endo*-phenylnorbornene, 59286-09-8.

References and Notes

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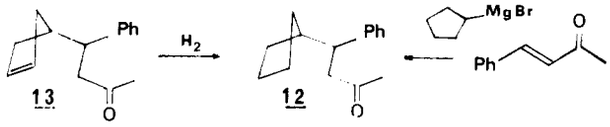

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(12) (a) Traces of other unidentified products were detected by VPC, but we never attempted to isolate them. Among them, there are certainly type II and cyclization products and CH_2CN adducts on the norbornene double bond.[13] (b) A preliminary experiment in benzene showed that the NI reaction quantum yield is lower than in acetonitrile (**7**, $\Phi = 0.24$; **8**, $\Phi = 0.15$) and that a compound ($\Phi = 0.12$) appeared having retention time which could correspond to an NII reaction product.
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(26) Just after submission of our manuscript, H. Sakuragi[25] has shown that the reactivity of the triplet states of the *O*-acyl oximes are correlated with their triplet energies.

Marine Natural Products: Sesquiterpene Alcohols and Ethers from the Sea Hare *Aplysia dactylomela*

Francis J. Schmitz,* Francis J. McDonald, and David J. Vanderah[1]

Department of Chemistry, University of Oklahoma, Norman, Oklahoma 73019

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Three isomeric sesquiterpene ethers, dactyloxene-A, -B, and -C, as well as a related alcohol, dactylenol, and its acetate were isolated from the sea hare *Aplysia dactylomela*. Structure determinations involved ^{13}C NMR, ^{1}H NMR in the presence of shift reagent, and chemical degradation. All of the compounds have a common rearranged monocyclofarnesyl skeleton. Dactyloxene-B and -C are stereoisomers, each having a tetrahydrofuran ring spiro-fused on a substituted cylohexene ring. Dactyloxene-A possesses an oxadecalin skeleton. Dactylenol was converted by acid treatment to a mixture containing dactyloxene-A and -C.

Earlier we described[2] the isolation of dactyloxene-B (**5**), a sesquiterpene ether having a rearranged monocyclofarnesyl skeleton, from the sea hare *Aplysia dactylomela*. Since then, other investigators studying marine red algae have discovered two alcohols[3] having the same carbon skeleton as **5** as well as two monobromo alcohols[4] and a related ether,[5] each having an unrearranged monocyclofarnesyl skeleton. One of the bromo alcohols has been synthesized by a biomimetic route utilizing bromonium ion induced cyclization of a farnesyl derivative.[6] In this paper we report the isolation and structure determination of four new monocyclofarnesyl sesquiterpenoids from *A. dactylomela*, all of which have the rearranged skeleton of dactyloxene-B (**5**). Two of these compounds are ethers, dactyloxene-A (**12**) and -C (**10**). The remaining compounds are an alcohol, dactylenol (**1**), and its acetate **4**. In addition to these sesquiterpenoids, extracts of *A. dactylomela* have also yielded a new bicyclic sesquiterpene alcohol, dactylol,[7] and two halogenated straight-chain acetylenic ethers,[8] one of which has shown interesting central nervous system activity.[9]

The sesquiterpene ethers **5**, **10**, and **12**, the related alcohol **1**, and the acetate **4** were isolated from hexane extracts of whole dried animals or dichloromethane solubles of an alcohol extract of fresh digestive glands of the sea hare. Chromatography of the hexane extracts over Florisil using hexane as eluent provided fractions containing dactyloxene-A, -B, and -C.

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